Observation of a Transition from BCS to HTSC-like Superconductivity in $Ba_{1-x}K_xBiO_3$ Single Crystals

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A study of temperature dependences of the upper critical field $B_{c2}(T)$ and surface impedance $Z(T) = R(T) + iX(T)$ in $Ba_{1-x}K_xBiO_3$ single crystals that have transition temperatures in the range $6 \le T_c \le 32$ K (roughly $0.6 > x > 0.4$) reveals a transition from BCS to unusual type of superconductivity. $B_{c2}(T)$ curves corresponding to the crystals that have $T_c > 20$ K have positive curvature (like in some HTSC), and those of the crystals with $T_c < 15$ K fall on the usual Werthamer-Helfand-Hohenberg curve. $R(T)$ and $X(T)$ dependences of the crystals with $T_c \approx 30$ K and $T_c \approx 11$ K are respectively linear (like in HTSC) and exponential (BCS) in the temperature range $T \ll T_c$. The experimental results are discussed in connection with the extended saddle point model by Abrikosov.

INTRODUCTION

$Ba_{1-x}K_xBiO_3$ compound undergoes a series of phase transformations on potassium doping. The base composition $BaBiO_3$ should be a metal with the half-filled conductivity band according to the band structure calculations [1]. However, it turns out to be an insulator due to the formation of a charge density wave (CDW), which distorts its perovskite lattice to monoclinic. The insulating state extends up to $x \approx 0.4$, while the monoclinic symmetry is changed by the orthorhombic one at $x \approx 0.13$. At the transition into metallic phase ($x > 0.4$) the lattice become cubic and no structural transitions is observed on further increase of x [2]. Deformations of the lattice are small and it remains quasi-cubic for the whole range of x.

Metallic $Ba_{1-x}K_xBiO_3$ is a superconductor. The superconducting transition temperature of optimally doped $Ba_{1-x}K_xBiO_3$ ($x \approx 0.4$) is rather large — $T_c \approx 32$ K, — and it is usually considered to be a HTSC. However, $Ba_{1-x}K_xBiO_3$ contains no transition metal atoms, has no counterparts for CuO_2 planes, and its properties are isotropic.

One of the striking features that are common for cuprate HTSCs and $Ba_{1-x}K_xBiO_3$ is the positive curvature of the upper critical field temperature dependence $B_{c2}(T)$ as determined by transport measurements. In the case of optimally doped $Ba_{0.6}K_{0.4}BiO_3$ it was observed in [3, 4], and, as noted in [5], the temperature dependences of $B_{c2}(T)$ of $Ba_{0.6}K_{0.4}BiO_3$ and $Tl_2Ba_2CuO_6$ [6] or $Bi_2Sr_2CaCuO_8$ [7] are coinciding if plotted in reduced scales. It is well-known that measurements of the upper critical field of HTSC using different methods produce inconsistent results; the same is true for $Ba_{0.6}K_{0.4}BiO_3$ [8, 9].

Another common property of cuprate HTSCs and $Ba_{1-x}K_xBiO_3$ is the linear dependence of both components of the complex surface impedance $Z(T) = R(T) + i\,X(T)$ on temperature in $T < T_c/2$ range [12], which is typical for d-wave symmetry of the order parameter. It is important to bear in mind that results concerning electromagnetic properties of $Ba_{1-x}K_xBiO_3$ are often conflicting because of difficulty of the production of high-quality samples: even $Ba_{1-x}K_xBiO_3$ crystals grown in the same conditions frequently differ in composition and homogeneity.

In the present paper we study evolution of $B_{c2}(T)$ dependences for a series of $Ba_{1-x}K_xBiO_3$ crystals ($0.4 < x < 0.6$) with T_c values from 32 to 6 K and find that as x decreases (which corresponds to increasing T_c) a transition from BCS to HTSC-like superconductivity takes place. The conclusion is confirmed by measurements of the surface impedance $R(T)$ and $X(T)$ in the highest quality crystals of $Ba_{1-x}K_xBiO_3$ with $T_c = 11$ K and $T_c = 32$ K.

SAMPLES AND EXPERIMENT

Making of high-quality single crystals of $Ba_{1-x}K_xBiO_3$ with uniform distribution of potassium at different values of x is a very difficult task. Our samples were grown by the electrochemical deposition method described in [10, 11]. The black with blue-green shine crystals had roughly cubic shape, well-defined faces, and volume ranging from 0.2 to 2 mm^3. We tried to obtain a series of crystals with different potassium content covering as wide range of the superconducting transitions temperatures T_c as possible, provided that the uniformity of composition within every crystal is maintained. Since even crystals originating from one batch have significant variation of T_c (sometimes as large as 10 K), all samples were preliminary tested by measurements of temperature dependences of ac susceptibility. Only samples with the narrowest and most regular superconducting transitions were selected for further experiments.

Measurement of ac susceptibility $\chi(T) = \chi' + i\chi''$ in application to superconductors is similar to the investigation of dc resistivity. In our case the frequency of the ac magnetic field excitation was 100 kHz and its amplitude was less that 0.1 Oe. Static external magnetic field

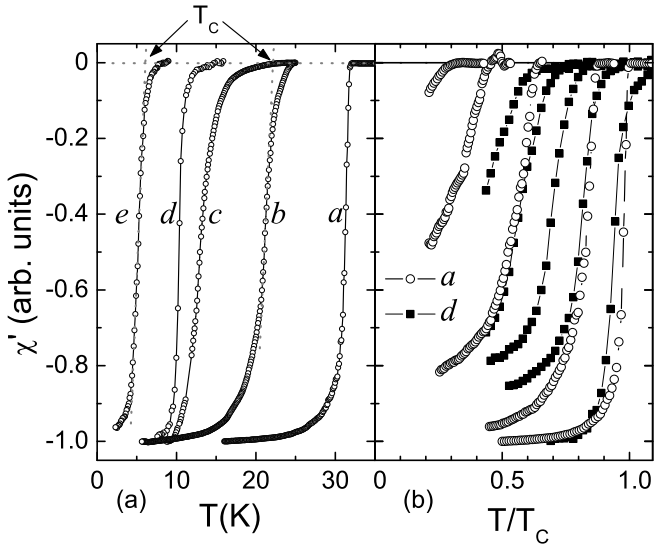

Figure 1: (a) Superconducting transition curves of $Ba_{1-x}K_xBiO_3$ crystals obtained by measurements of ac susceptibility $\chi'(T)$. The definition of the transition point, which is used in the paper, is shown for samples b and e; (b) the effect of magnetic field B on $\chi'(T)$ curves of the crystals (circles) a and (squares) d. The field values (from left to the right) for sample a : $B = 0$, 1, 6, 12 and 19.5 T; for sample d: $B = 0$, 0.067, 0.133, 0.2 and 0.27 T. Data for sample a are from the paper [4]

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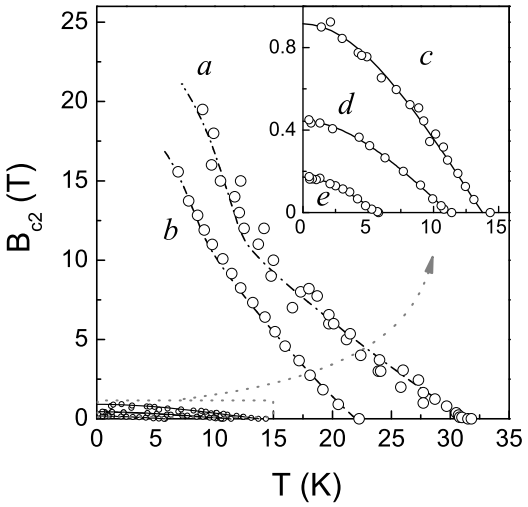

Figure 2: The upper critical field of samples $a - e$. Dash-dot lines present $B_{c2}(T)$ dependences calculated using the extended saddle point model [16]. The inset shows zoom in of the left lower corner of the main graph. Solid lines are theoretical BCS curves.

up to 17 T was applied using superconducting magnet perpendicularly to the measuring field. Samples were not orientated in any special way in respect to the field, though we checked that results were reproducable for different positions of the crystals. T_c point was determined from the transition curve as an intersection of the tangent that was drawn at the inflexion point and zero level that corresponds to the normal state (see Fig. 1a).

Temperature dependences of the surface impedance $Z(T)$ were measured using the resonance technique described in [13] at $\omega/2\pi = 28.2$ GHz in 0.4-120 K temperature range. H_{011} mode of a cylindrical niobium resonator was employed (the quality factor of the empty resonator was $\approx 2 \cdot 10^6$ in all operating temperature range); amplitude of the high-frequency magnetic field was less than 1 Oe. The experimental setup and method of measurements are described in details in [14].

RESULTS

Temperature dependences of the real part of ac susceptibility $\chi'(T)$ for all samples with different potassium doping level that are studied in the present paper are shown in Fig. 1a. (The transition temperature decreases with increasing x.)

The superconductivity is suppressed when magnetic field B is applied. It is illustrated in Fig. 1b for samples a (the data for this sample are taken from paper [4], that we published earlier) and d. Remarkably, in spite of tremendous, more than ten times, difference of the field magnitudes $\chi'(T)$ curves of these samples that correspond to the same reduced temperatures T/T_c have about the same relative transition width and in general are similar to each other. This fact is important, because there is no method to find T_c point from a non-zero-width transition curve that has a rigorous theoretical foundation. The method we employ (Fig. 1a) is widespread, but it is still possible that it introduces a systematic error. Figure 1 strongly suggests that this error, if any, is identical for different samples.

$B_{c2}(T)$ curves for all samples studied are shown in Fig. 2. For crystals c, d, and e with $T_c = 14$, 11, and 6 K $B_{c2}(0)$ does not exceed 1 T and the curvature of $B_{c2}(T)$ is negative. Temperature dependences of the upper critical field of these samples are in complete agreement with the BCS model. The estimations of the coherence length using formula $B_{c2}(0) = \Phi_0/(2\pi\xi(0)^2)$ give $\xi(0) = 20$, 30, and 40 nm for samples c, d, and e respectively.

$B_{c2}(T)$ curves of crystals a and b ($T_c = 32$ and 22 K) have positive curvature. The upper critical fields at $T = 0$ are dozens of times higher than that for crystals c, d, and e, though available data are insufficient to make even rough estimation of their magnitude. At the very least, $B_{c2}(0)$ of sample a is higher than 25 T, so $\xi(0)$ is no more than 4 nm. Dash-dot lines in Fig. 2 are plotted according to the Abrikosov theory [15, 16]. The curves are obtained by numeric solution of Eq.(15) from [16] using the following parameters (for notation see [16]): $\eta = 1$, $\alpha = 4\pi m_x T_c/\mu_1 m_e = 0.8$ for sample a; and $\eta =$

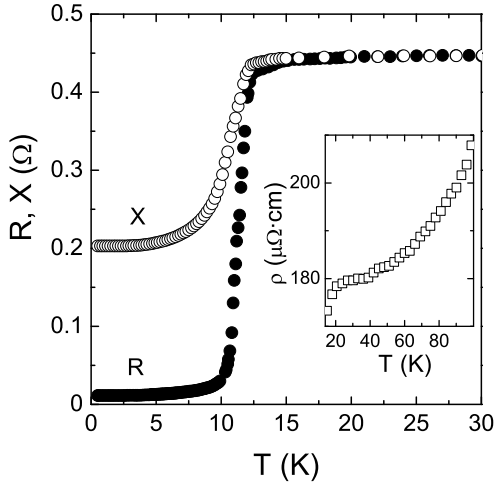

Figure 3: Surface resistance $R(T)$ and reactance $X(T)$ in superconducting and normal (fragment) states of sample d at 28.2 GHz. The inset shows $\rho(T)$ dependence in $10 < T \leq 100$ K range.

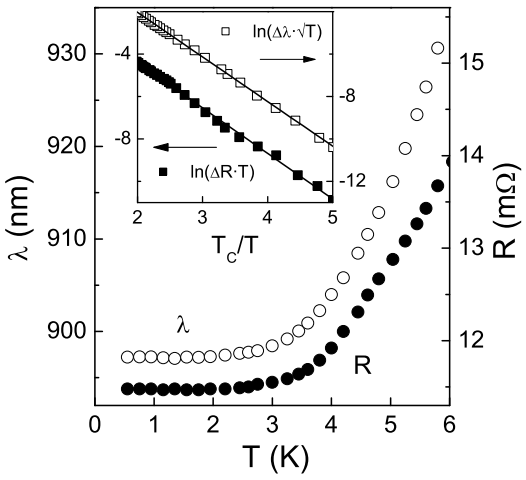

Figure 4: $R(T)$ and $\lambda(T) = X(T)/\omega\mu_0$ of sample d at low temperature. The inset shows logarithms of (solid squares) $T\Delta R(T) = T[R(T) - R_{res}]$ and (open squares) $\sqrt{T}\Delta\lambda(T) = \sqrt{T}[\lambda(T) - \lambda(0)]$ in comparison to (solid lines) the predictions of the BCS model; their slope gives the gap value $\Delta(0)$.

0.9, $\alpha = 1.2$ for sample b [17].

$B_{c2}(T)$ curves shown in Fig. 2 demonstrate that the nature of superconductivity in $Ba_{1-x}K_xBiO_3$ is changed with the increase of potassium doping: it turns from an unusual one to the standard BCS kind.

Microwave measurements confirm this conclusion. This technique reveals another important measure of superconducting sample quality beside the width of superconducting transition — the residual surface resistance $R_{res} = R(0)$. It is well-known that the low-temperature features of the surface impedance $Z(T)$ in the imperfect crystals are masked by high level of the residual losses, so they can be observed only in samples with the lowest values of R_{res}. In the present work, only one of the samples studied, sample d, satisfies this selection criteria. Temperature dependences of the impedance components for this crystal are shown in Fig. 3. For $T > T_c$ the normal skin effect condition $R(T) = X(T)$ is fulfilled, so the temperature dependence of the resistivity $\rho(T) = 2R^2(T)/\omega\mu_0$ can be derived; it is shown in the inset. Low-temperature parts of $R(T)$ and $\lambda(T) = X(T)/\omega\mu_0$ curves are shown in Fig. 4. In the same way as in classical superconductors, the resistance $R(T)$ of sample d saturates at temperature-independent level of the residual losses $R_{res} \approx 11.5$ mΩ for $T < T_c/4$ and the field penetration depth reaches $\lambda(0) \approx 900$ nm at $T \to 0$. As shown in the inset of Fig. 4, both quantities approach saturation levels exponentially, in complete agreement with the BCS theory: $R(T) \propto (1/T)\exp(-\Delta_0/kT)$, $\lambda(T) \propto (1/\sqrt{T})\exp(-\Delta_0/kT)$, where Δ_0 — is the superconducting gap at $T = 0$. The values of Δ_0 derived from these curves agree well and give $\Delta_0 \approx 2.1\, k_B T_c$, which means that the electron-phonon coupling constant in $Ba_{1-x}K_xBiO_3$ is not small. Using well-known BCS equations, we obtain a number of sample parameters: the relaxation time $\tau \approx 6 \cdot 10^{-13}$ s at $T = T_c$, average Fermi velocity $v_F \approx 3 \cdot 10^5$ m/s (which is about 3 times less than the value following from the band structure calculations [1]), and carrier mean free path $l \approx 180$ nm. According to these estimations crystal d is a clean London superconductor.

Surface impedance of the optimally doped $Ba_{0.6}K_{0.4}BiO_3$ crystal ($T_c \approx 30$ K) was measured at 9.4 GHz in our paper [12]. Similar to the case of tetragonal HTSCs, we observed practically linear temperature dependences of $\lambda(T)$ and $R(T)$ for $T < T_c/2$ [12, 13]; their extrapolations to $T \to 0$ give $\lambda(0) \approx 300$ nm and $R_{res} \approx 10$ mΩ.

Hence, microwave measurements confirm that the nature of superconductivity of samples with $T_c = 11$ K and optimally doped samples is fundamentally different: the former are BCS-type superconductors, and the latter resemble cuprate HTSCs.

DISCUSSION

The origin of the transition from HTSC-like to BCS superconductivity in $Ba_{1-x}K_xBiO_3$ compound, which is revealed in the present paper, should be sought in transformation of its crystal and electronic structure.

According to the hypothesis [10, 11], $Ba_{1-x}K_xBiO_3$ is formed from the homologous series of oxides $Ba_nBi_mO_y$ by means of potassium intercalation. Lattice of the oxides consists of alternating BiO_2 and BaO layers that form a supercell, which size depends on the ratio $n : m$. Potassium is intercalated into $Ba_nBi_mO_y$ between adjacent BiO_2 layers ("a bismuth planes") leading to increase in the number of Bi ions with the oxidation level 5+ in

these layers. As a result $Ba_nK_{m-n}Bi_mO_{3m}$ composition is formed, meaning that x cannot assume an arbitrary value but solely those that correspond to a rational fraction $n : m$ of Ba and Bi content. As shown in [19], the anisotropic $Ba_nBi_mO_y$ matrix has a mosaic structure at microscopic level, its lattice consists of ordered blocks that are displaced by a period of quasi-cubic lattice. When the fraction $n : m$ goes down, the block size decreases and the layered structure completely disappears at $n : m = 1 : 2$. If these results are applied to $Ba_{1-x}K_xBiO_3$, then we find that a truly isotropic phase is formed at $x = 0.5$ ($n : m = 1 : 2$) instead of $x = 0.4$ ($n : m = 3 : 5$). Local lattice anisotropy was indeed observed in $Ba_{0.6}K_{0.4}BiO_3$ by electron microscopy [18]. It is not observed in macroscopic properties probably because of the mosaic lattice structure and easy twinning, i.e., because of the absence of long-range order in the positions of potassium.

The arrangement of potassium into layers and related modification of the oxidation level of Bi ions in the adjacent bismuth layers leads to modulation of space charge. In the case with the long-range order (for $n/m \sim 1$) it signifies formation of the charge density wave (CDW). The very CDW is responsible for insulating state of $Ba_{1-x}K_xBiO_3$ for $x < 0.4$. As the size of lattice blocks of $Ba_nBi_mO_y$ matrix decreases, the long-range order disappears, but the "charge-density wave" is preserved at microscopic level defining the short-range ordering of potassium until the layered structure of the matrix is completely destroyed. According to this concept, a residual influence ("traces") of CDW should be retained in the metallic phase of $Ba_{1-x}K_xBiO_3$ in the potassium content range from $x = 0.4$ to 0.5. Indeed, such traces were observed in the Compton positron scattering [20] and IR conductivity [21] experiments. Since high-temperature superconductivity in $Ba_{1-x}K_xBiO_3$ is observed roughly in the same composition region, it is possible that the traces of CDW play a crucial role in its origin.

A connection between the influence of CDW and superconductivity may be established within the Abrikosov model [15]. According to it many features of HTSC including the high transition temperature, d-wave pairing symmetry, and positive curvature of $B_{c2}(T)$ can be explained if the electronic spectrum contains an extended saddle point (i.e., a flat piece of the equipotential surface) and the Fermi energy is close to it. Suitable conditions in $Ba_{1-x}K_xBiO_3$ can be formed because of the influence of CDW. According to [20] the traces of CDW are manifested as a suppressed electron density of states near the middle of diagonal of the Brillouin zone (point L); it is exactly where the Fermi surface is located at $x = 0.4$ [1]. Assuming that the suppression forms a flat part of the spectrum, we can apply the Abrikosov model to explain all our observations: (i) the linear temperature dependences of $\lambda(T)$ and $R(T)$ follow from d-wave symmetry of the order parameter, and (ii) the upper critical field

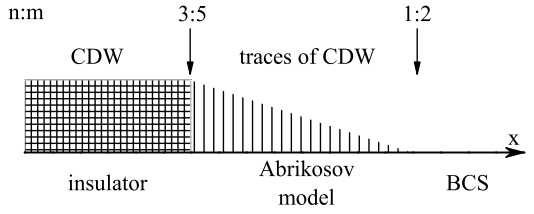

Figure 5: The hypothetical phase diagram of $Ba_{1-x}K_xBiO_3$. Ba to Bi content ratios $n : m$ that correspond to presumed phase boundaries are indicated.

curves of samples a and b fit the theoretical dependences well.

The Abrikosov model has a key advantage in respect to application to $Ba_{1-x}K_xBiO_3$: the dominating pairing mechanism both in the Abrikosov and BCS models is the electron-phonon interaction. Therefore, a transition from one model to another can occur naturally.

The framework we propose is illustrated by the diagram in Fig. 5. At small x the long-range order in positions of Bi^{5+} ions in the crystals is maintained, so the charge density wave, which opens a gap at the Fermi surface, is present and the compound is an insulator. At the transition into superconducting metallic phase at $x = 0.4$ ($n : m = 3 : 5$) the long-range order disappears, but, presumably, a short-range ordering of bismuth ions with different oxidation levels is preserved. It is manifested in various "traces" of the charge density wave, one of which can be flat parts of the spectrum formed due to the suppression of the density of states in the L points in the Brillouin zone. Such flat parts of the spectrum put into play the Abrikosov model and leads to the high transition temperature, d-wave symmetry of the order parameter (and, consequently, to linear temperature dependences of $\lambda(T)$ and $R(T)$), and positive curvature of $B_{c2}(T)$. On further increase of x simultaneously the short-range order is destroyed and the Fermi surface contracts and move away from the degenerate point of the Brillouin zone. Because of one or both of these reasons the Abrikosov mechanism eventually breaks down, but the electron-phonon coupling make sure that the superconductivity remains, now within the BCS model. If the latter transition is caused by complete loss of the short-range order (disappearance of traces of CDW), then it probably takes place at $n : m = 1 : 2$ ($x = 0.5$).

CONCLUSIONS

To conclude, $Ba_{1-x}K_xBiO_3$ compound is a unique object exhibiting a transition from HTSC to BCS superconductivity with the increase of potassium doping x in the metallic phase ($x > 0.4$). We observe it clearly in measurements of temperature dependences of the upper critical field $B_{c2}(T)$ and surface impedance $Z(T)$ of a

series of $Ba_{1-x}K_xBiO_3$ single crystals. The change of the nature of superconductivity can be due to special features of electron spectrum of $Ba_{1-x}K_xBiO_3$ that are related to residual influence of the charge density wave and employment of the high-temperature superconductivity mechanism suggested by Abrikosov [15].

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